Developing Scanning Electrochemical Microscopy (SECM) for Cathode Interfaces

Robert C. Tenent
National Renewable Energy Laboratory
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DOE Vehicle Technologies Program
2019 Annual Merit Review and Peer Evaluation Meeting

Project ID # bat410

Overview

Timeline

- Project start date: 10/01/2018
- Project end date: 9/30/2021
- Percent complete 16%

Barriers

- Barriers addressed
  - Performance
  - Life
  - Cost

Budget

- Total project funding: $1.46M
  - DOE share: $1.46M
  - Contractor share: $90K
- Funding for FY 2017 $0
- Funding for FY 2018 $463,976

Partners

- New Mexico State University
- National Renewable Energy Lab

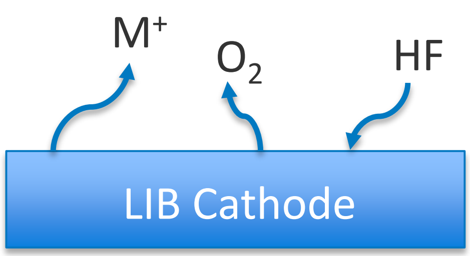
Professor Hongmei Luo
New Mexico State University

Robert Tenent
NREL

Chaiwat Engtrakul
NREL

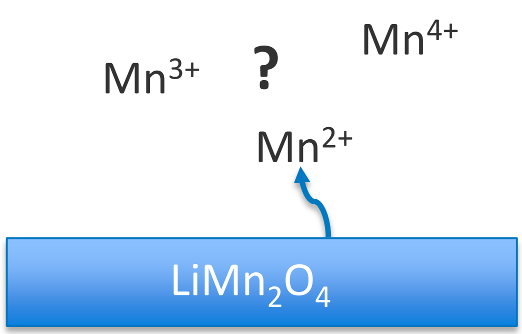
Relevance

Several processes occurring at the cathode/electrolyte interface impact performance and lifetime of lithium ion batteries (LIBs)



- Metal Dissolution
- Oxygen Evolution
- HF attack

Despite intensive study, many mechanistic questions remain about some of these ”well known” processes



Post mortem analysis of electrodes and electrolytes have been useful tools to understand these processes, however these techniques may not detect short lived species generated immediately at the electrode/electrolyte interface

A need exists to develop near-surface, in-situ diagnostics to help unravel mechanistic details of these processes

Approach

Scanning Electrochemical Microscopy (SECM) as well as other electrochemical probe microscopies enable a myriad of techniques for in-situ analysis of processes occurring at the electrode/electrolyte interface

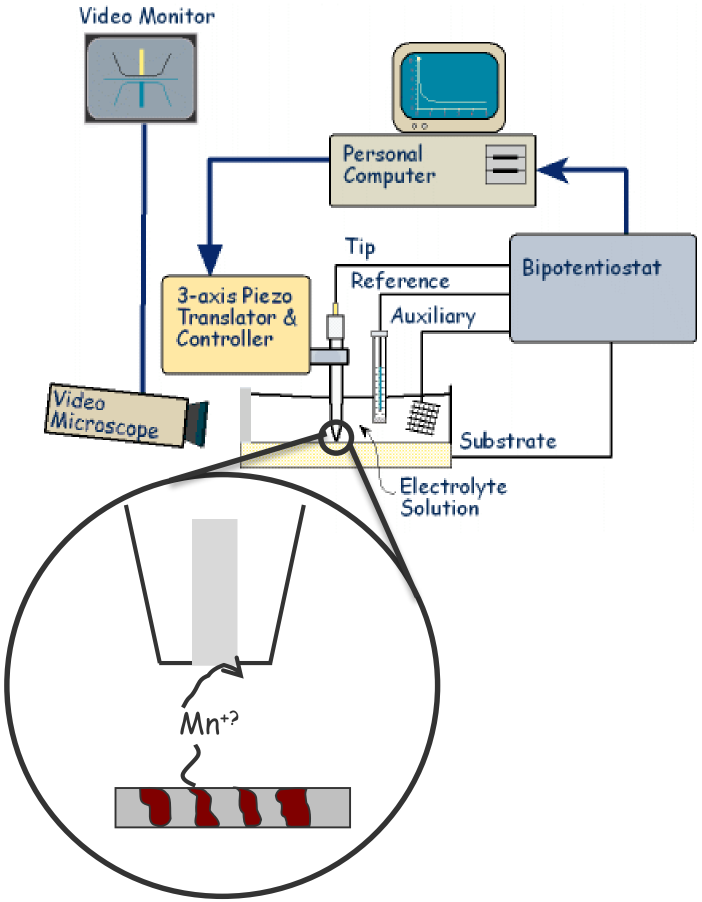
Conceptually similar to other probe microscopies

Measured signal due to electrochemical processes occurring between the probe “tip” and an underlying substrate

High speed electrochemical analysis protocols allows observation of short-lived reactive species driving interface degradation processes

Imaging capabilities allow spatial observation of surface processes

Initial work will focus on degradation processes of $LiMn_2O_4$

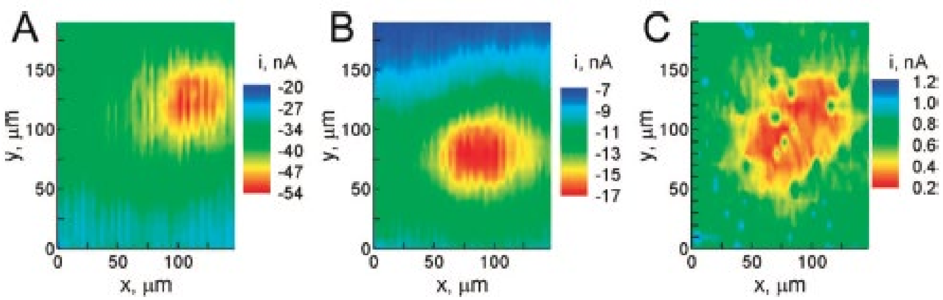


Approach

SECM methods have previously been shown to enable imaging of selected species evolving from various substrates as well as localized characterization of pH at an electrode surface

We will adapt these methods specifically for LIB cathode interfacial process analysis

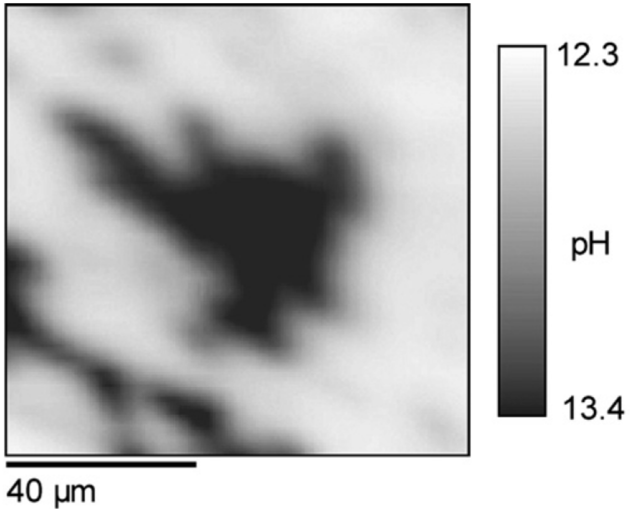
SECM combined with voltammetric techniques can enable differentiation of species evolving from electrode surface



Example data shows images of Pb(A), Cd(B) and O_2 (C) evolving from a model substrate.

Mario A. Alpuche-Aviles, John E. Baur, and David O. Wipf
Anal. Chem. 2008, 80, 3612–3621

SECM pH map produced on model substrate with IrO_2 tip electrode



Emad El-Deen M. El-Giar and David O. Wipf
J. Electroanal. Chem. 2007, 609, 147-154

FY19-Milestones

Milestone Name/Description	End Date	Type
Development of baseline thin film cathode material samples ($Li_xMn_2O_4$) for further study including initial characterization.	12/29/2018	Complete
Initial demonstration of bench level quantitation and differentiation of degradation from baseline model materials.	3/30/2019	Complete
Complete SECM system modifications and re-design for use with lithium ion battery materials under inert atmosphere.	6/29/2018	On Schedule
Final report on SECM based analysis of Mn-dissolution on baseline model materials.	9/30/2018	Annual Milestone (Regular)

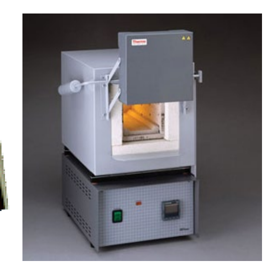
Development of Model Cathode Interfaces

Vacuum Deposition

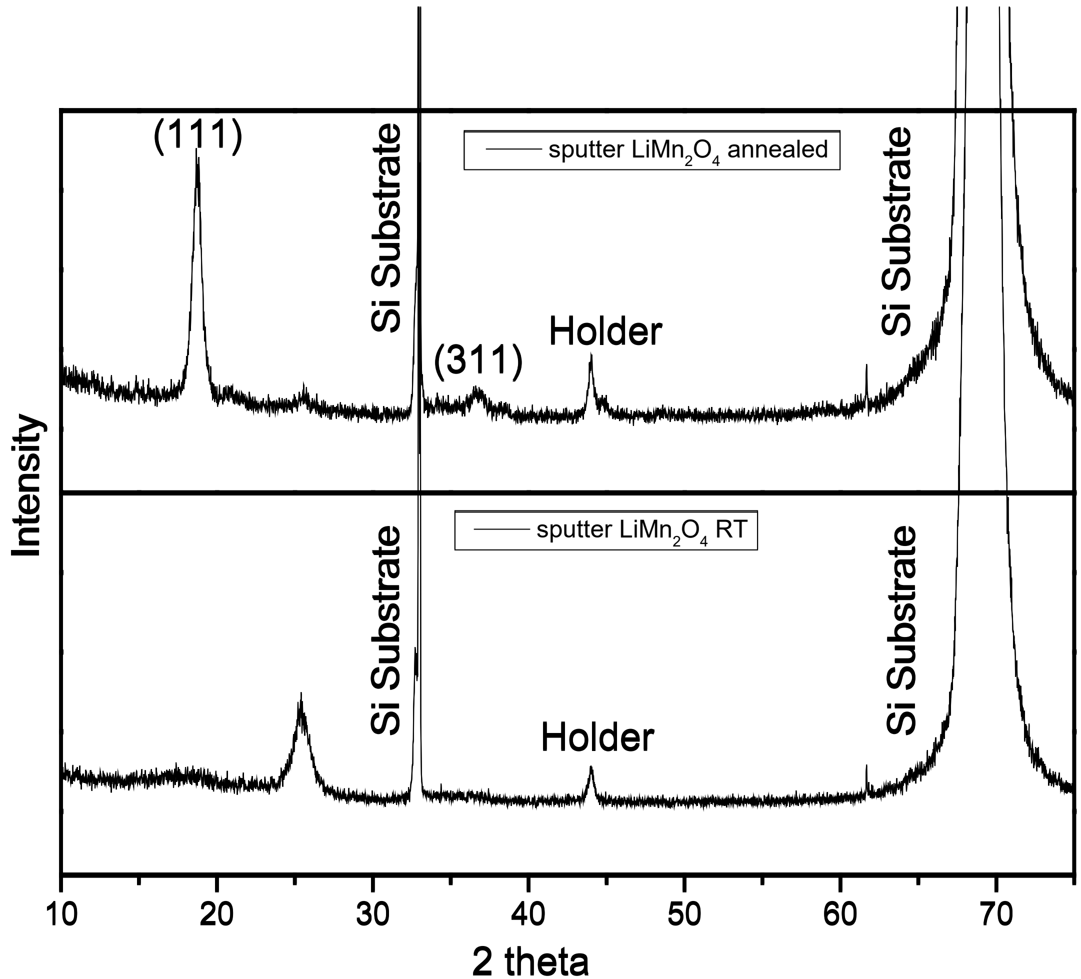
- Co-sputter deposition, 3 magnetrons for RF/DC sputtering
- Five thermal evaporation sources
- Air sensitive samples handled/stored under inert atmosphere

Polymer Assisted Deposition (PAD)

- Aqueous processing - metal precursors with water-soluble polymers
- Deposit films of nearly <u>any</u> *metal-oxides* with desired structural and physical properties
- Control of solution stability, reactivity, and processibility



Sputtering Deposition of $LiMn_2O_4$



<u>Deposition Conditions</u>

Target: 2" $LiMn_2O_4$

Power: 90W

Pressure: 15 mTorr

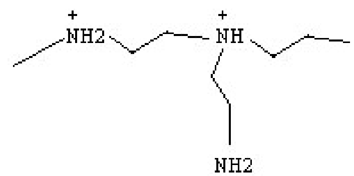
Gas: Ar/O_2 (1:1) @ 10 sccm

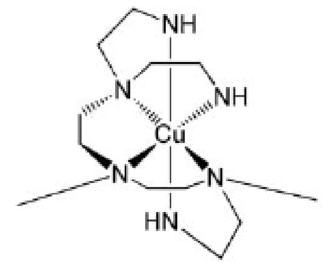
Room temperature sputtered film does not form $LiMn_2O_4$ phase

Sputtered film annealed at 600C for 3 h forms $LiMn_2O_4$ phase

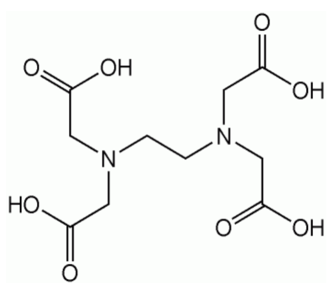
PAD Chemistry Overview

metal nitrate, metal chloride, metal hydroxide

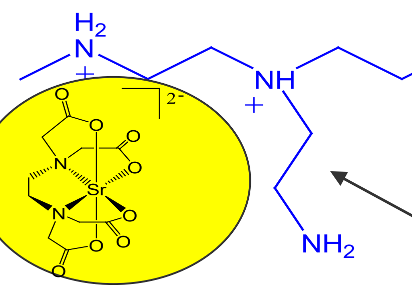




PEI (polyethyleneimine)



EDTA (ethylenediaminetetra acetic acid)



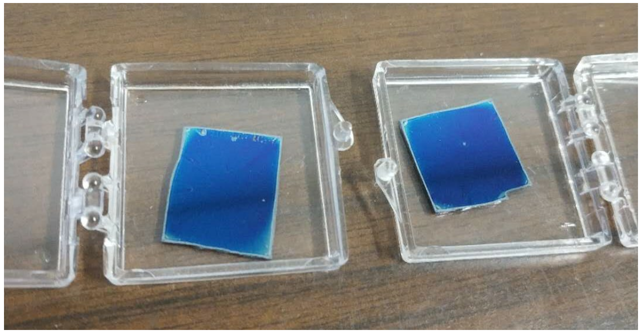
Sr bound to PEI as an EDTA complex

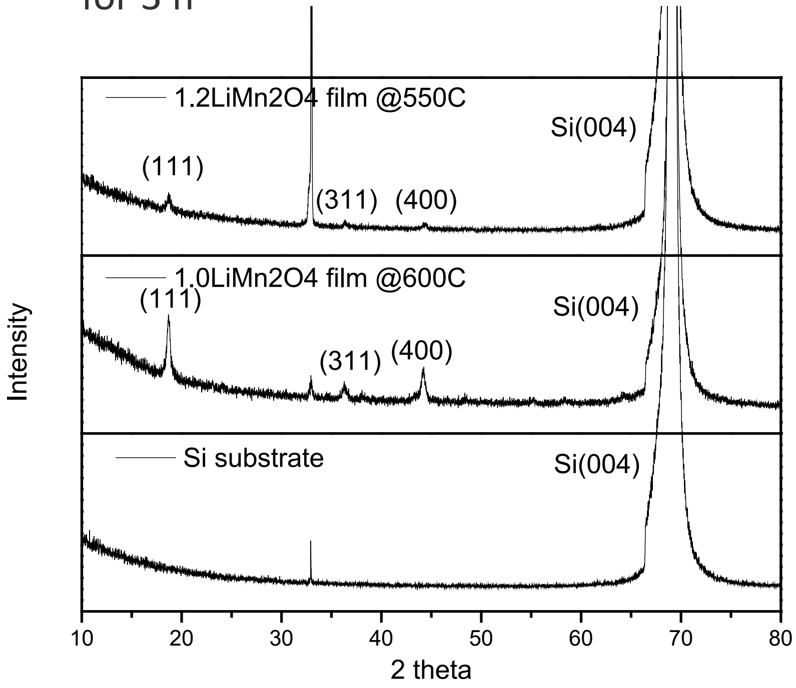
PAD solution stable for years

Burrell, et al, *Chem. Commun.* 1271 (2008).

PAD of $LiMn_2O_4$

1. Mixing lithium nitrate, manganese acetate, DI water, EDTA and PEI, stirring until solution becomes clear and homogenous
2. Spin-coating precursor solutions at 3000 rpm for 30 s;
3. Annealing in air to 550 ºC or 600 ºC for 3 h

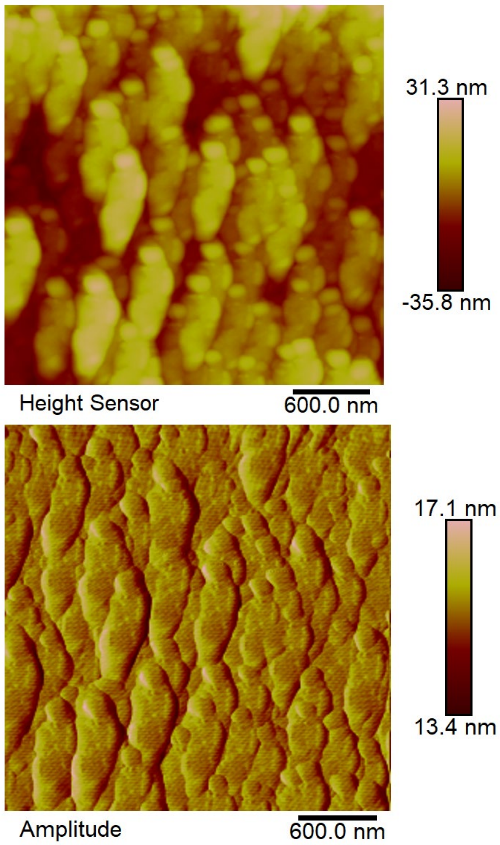




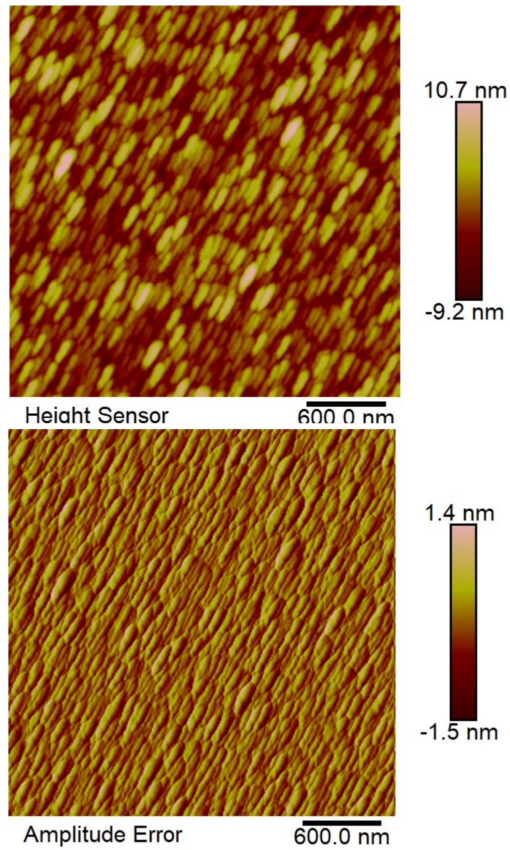
- Peaks (111), (311), (400) are observed, attributed to $LiMn_2O_4$.
- No impurity phases are observed.
- Higher crystallinity for film annealing at 600C than 500C.

This technique has also been previously demonstrated for various NMC compositions

PAD Produces Low Surface Roughness Films



$Li_{1.2}Mn_2O_4$ @ 550C

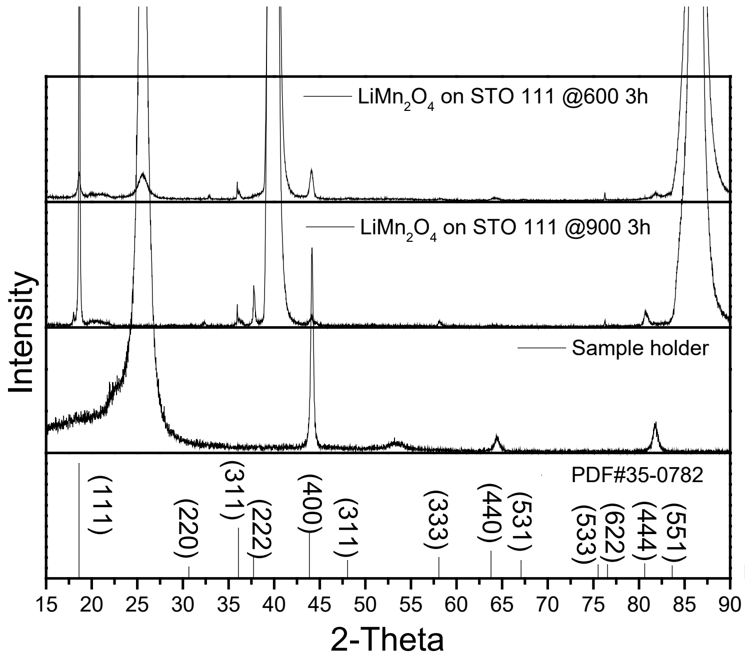


$LiMn_2O_4$ @ 600C

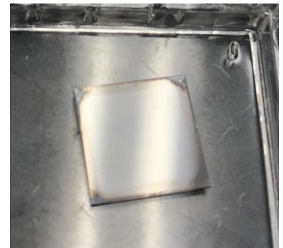
Sample of $LiMn_2O_4$ @600C is very smooth, roughness less than 3nm

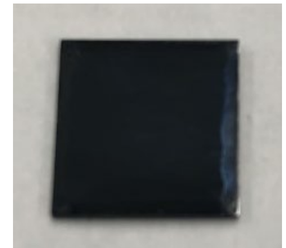
PAD Enables Growth of Epitaxial Films on Planar Substrates

XRD of $LiMn_2O_4$ and $LiNi_{0.5}Mn_{1.5}O_4$ from PAD on STO 111 Substrates

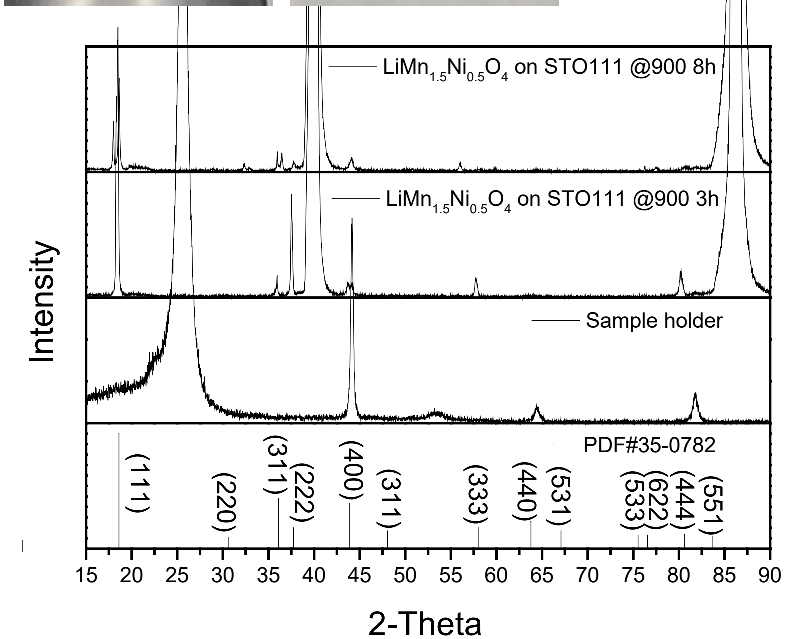


STO | Nb-STO





10mm by 10mm PAD films of $LiMn_2O_4(111)$

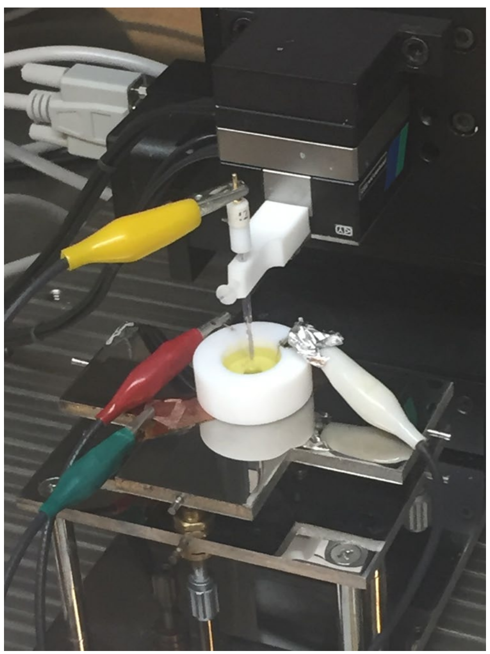


Annealing temperatures of 600 and 900C explored as well as varied annealing times.
Higher temperature improves epitaxy, but can also lead to degradation
Currently exploring optimized conditions to get epitaxial films

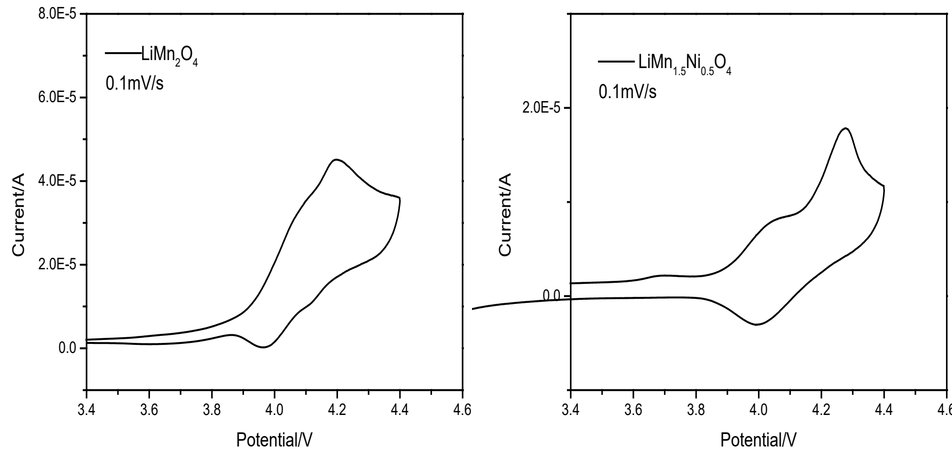
Electrochemical Analysis of PAD Materials

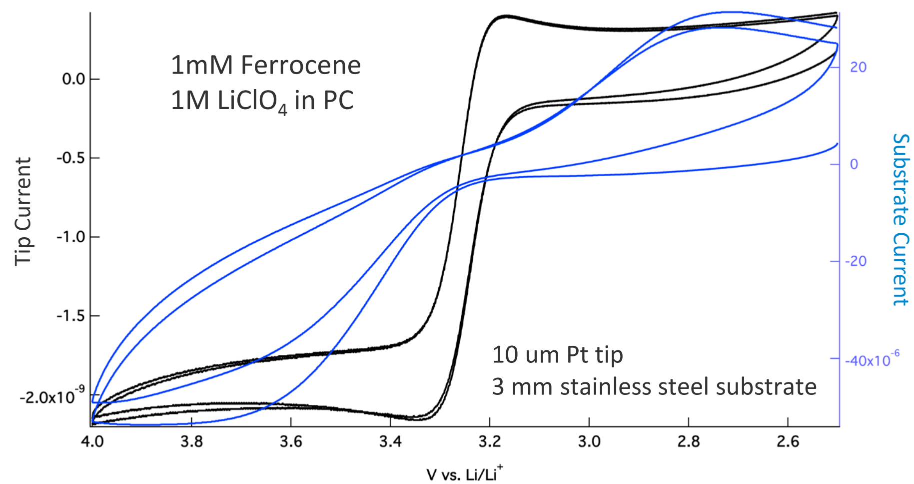
The SECM unit has been installed in new NREL Electrochemistry Laboratory

Initial instrument testing has shown excellent performance in glovebox environment



Cyclic voltammetry of PAD films in Gen 2 electrolyte



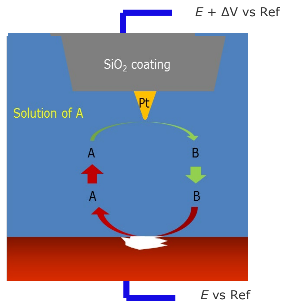


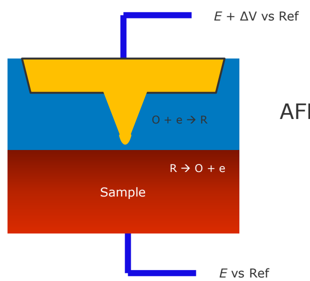
Initial testing under inert conditions shows excellent signal quality

Combined AFM/SECM Enables High Resolution Imaging

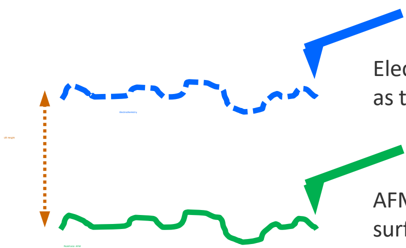
NREL microscopy group is purchasing a combined SECM/AFM

Feedback mode





AFM mode



Electrochemical signal measured as tip tracks above surface

AFM mode used to determine surface topography

SECM/AFM will be used to obtain high resolution data on samples in later stage of work

Any proposed future work is subject to change based on funding levels

Combination of high resolution topography with electrochemical data helps identify source of feedback signal without diffusional broadening effects of electrochemical feedback loop

"Conventional" SECM experiments will still be employed for fundamental studies of feedback processes and initial characterization of evolving species

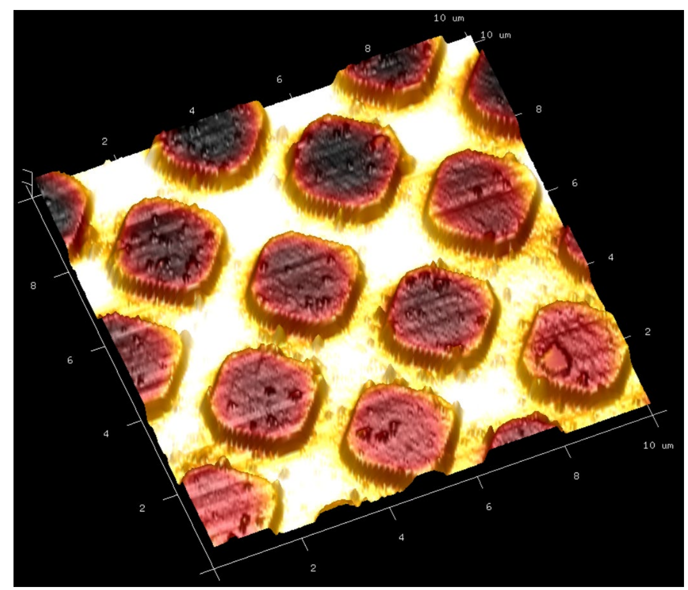


Image showing overlay of topography and tip feedback current

Responses to Previous Year Reviewers' Comments

- N/A - New project in FY19

Collaboration and Coordination

- New Mexico State University
- National Renewable Energy Lab
- Will expand collaborations with other VTO program partners as work progresses

Remaining Challenges and Barriers

- Studies of initial simplified model systems are just beginning. We expect application of our techniques to more complex industrially relevant materials (NMC cathodes) will present additional challenges including overlapping degradation processes.
- While SECM is capable of performing rapid electrochemical analysis near an active cathode/electrolyte interface the spatial mapping capabilities can be limited by tip size and mediator diffusion.

Proposed Future Research

- SECM generation/collection studies of $LiMn_2O_4$ interfaces at high voltage with varied electrolyte formulations.
- Voltammetric analysis at tip electrodes near an actively degrading $LiMn_2O_4$ substrate to deconvolute overlapping processes.
- SECM generation/collection studies of $LiNi_{0.5}Mn_{1.5}O_4$ as model system progressing toward NMC cathodes.
- Transfer of electrochemical measurement methods to AFM/SECM to obtain high resolution mapping of degradation processes.
- Eventual studies of NMC cathode materials.

Any proposed future work is subject to change based on funding levels

Summary

- PAD and vacuum deposition methods have been used to deposit initial model materials samples. These samples appear to be functioning as expected and are still undergoing further characterization including battery testing.
- We are exploring the synthesis and deposition of planar single crystal samples of $LiMn_2O_4$ and $LiNi_{0.5}Mn_{1.5}O_4$ as example materials for SECM work as well as potential use across the broader program.
- The SECM system has been installed in the new NREL Electrochemical Research Lab.
- NREL has ordered a new combined SECM/AFM. Our team advised NREL microscopy staff on acquisition and will collaborate with this team to obtain higher resolution imaging when appropriate.

Thank You

www.nrel.gov

robert.tenent@nrel.gov

linkedin.com/in/rctenent

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